

A2b

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY

(51) International Patent Classification 3 : B01D 17/04		A1	(11) International Publication Number: WO 83/01208 (43) International Publication Date: 14 April 1983 (14.04.83)
<p>(21) International Application Number: PCT/US82/01311</p> <p>(22) International Filing Date: 24 September 1982 (24.09.82)</p> <p>(31) Priority Application Numbers: 307,300 419,303</p> <p>(32) Priority Dates: 30 September 1981 (30.09.81) 20 September 1982 (30.09.82)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: RADIAN CORPORATION [US/US]; PO Box 9948, 8501 Mo-Pac Boulevard, Austin, TX 78766 (US).</p> <p>(72) Inventor: BEALL, Gary, W.; 11814 Rustic Lane, Austin, TX 78750 (US).</p> <p>(74) Agent: KLAUBER, Stefan, J.; Weingram & Klauber, East 210 Route 4, Paramus, NJ 07652 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: METHOD OF BREAKING EMULSIONS</p>			
<p>(57) Abstract</p> <p>A method for treating polar or aqueous fluid emulsions of an organic composition. The method comprises contacting the emulsion with an emulsion-breaking amount of an organoclay to adsorb a major portion of the organic composition. Preferably, a portion of the water or polar fluid is then removed.</p>			

(57) Abstract

A method for treating polar or aqueous fluid emulsions of an organic composition. The method comprises contacting the emulsion with an emulsion-breaking amount of an organoclay to adsorb a major portion of the organic composition. Preferably, a portion of the water or polar fluid is then removed.

Best Available Copy

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US82/01311

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, so state)	
According to International Patent Classification (IPC) or to both National Classification and IPC	
INT. CL. 3 B01D 17/04	
U.S. CL. 210/708; 252/323	

II. FIELDS SEARCHED

Fields of Document Search	
Classification System	Classification Symbols
U.S.	210/679,680,691,708,908,924 252/323,428,430
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included - the Fields Searched:	

III. DOCUMENTS CONSIDERED TO BE RELEVANT¹⁴

Category ¹⁵	Citation of Document ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. 18
A	US, A, 2,015,260, (DeGROOTE), 24 SEPTEMBER 1935.	1-10
A	US, A, 2,367,384, (TYMSTRA), 16 JANUARY 1945.	1-10
A	US, A, 3,046,233, (LEVY), 24 JULY 1962.	1-10
A	US, A, 3,487,928, (CANEVARI), 06 JANUARY 1970.	1-10

* Special categories of cited documents:¹⁹

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search²⁰

28 DECEMBER 1982

Date of Mailing of this International Search Report²¹

06 JAN 1983

International Searching Authority²²

ISA/US

Signature of Authorized Officer
Ivars C. Cintins

Description

Method of Breaking Emulsions

Related Applications

5 This application is a continuation-in-part of my copending application Serial No. 307,300, filed on September 30, 1981, and entitled "Organoclay Waste Disposal Method." The entire disclosure of this parent application is incorporated herein by reference.

Background of Invention

10 Technical Field:

This invention relates to a method for breaking emulsions of an organic composition and water or a polar fluid, and is particularly useful in the treatment of waste fluids.

15 Background Art:

One of the major problems facing cities, chemical manufacturers, and industries using various chemicals, is waste disposal. More particularly, cities and industries are often faced with the disposal of emulsions of organic contaminants. Typically, these are aqueous 20 emulsions; however, there exists waste fluids which are emulsions of organic contaminants and polar fluids. In many of these operations, the disposal of water contain-

ing the contaminant substances is a problem. Regulations make it impossible to simply dump such waste water into streams, even if such method of disposal were desirable. Various methods have been proposed for removing such contaminants from waste water, but they have been relatively expensive or inefficient. Therefore, the removal of the contaminants from aqueous solutions, and in particular from waste water containing small amounts, is a problem which has not been completely solved.

It is often desirable to dispose of such waste fluids by reducing the volume of the fluid. When emulsions exist, this is often difficult to do, because prior to reducing the volume of the waste fluid, it is necessary to break the emulsion. Indeed, while it is often desirable to incinerate emulsions to dispose of them, such a process is normally very expensive due to the water present in the emulsion. This problem may be eliminated by breaking the emulsion to remove the water. Once the volume of the waste fluid is reduced, various means may be utilized to dispose of the remaining waste such as incineration or see, for example, assignee's co-pending application, U.S. Serial No. , filed on September 7, 1982, and entitled "Method of Immobilizing Organic Contaminant and Non-Flowable Matrix Produced Therefrom." This co-pending application relates to a method for treating waste fluids containing organic contaminants to solidify them in order to facilitate disposal. Prior to such solidification, however, it is desirable in some instances where emulsions are present, to reduce the volume of such fluid by breaking the emulsion and removing a portion of the water (or polar fluid) contained therein.

There exists numerous methods for breaking emul-

sions, typically oil and water emulsions. See for example the following U.S. patents:

2,367,384 to Tymstra;
2,937,142 to Rios;
5 3,196,619 to Shock;
3,487,928 to Canevari;
3,528,284 to Skoglund et al;
3,986,953 to Beaucaire;
10 4,231,866 to Moser et al; and
4,279,756 to Weiss et al

More specifically, Tymstra describes a method for removing small quantities of water-immiscible organic oily impurities from water. The method consists of 15 contacting the oily composition with an inert solid coated with a cation surface-active bonding agent. The solid employed may be beach sand, mud flat deposits, silt, clay, limestone, silica, rice hulls, etc. The cationic surface-active bonding agent may be quaternary 20 ammonium, phosphonium, arsonium, or primary, secondary, or tertiary organic amines or salts thereof. This reference does not teach or suggest the use of the specific organoclays utilized herein to break emulsions, nor the unexpected efficiencies of these clays in breaking 25 emulsions.

Rios separates phenolic substances from aqueous solutions by contacting the aqueous solution with a clay adsorbent. The clay is previously treated by depositing carbonaceous material thereon, and then subjecting it to 30 combustion regeneration to burn off the carbonaceous material.

Canevari separates droplets of oil from an aqueous phase, using a mixture comprising a sodium montmorillon-

ite clay and an organic cationic agent or glycol. The organic cationic agent is preferably an amine. The mixture is applied as a flocculating clarifying solution containing from 1 to 5% of clay to water, and an effective amount of the organic cationic agent or glycol.

Beaucaire describes breaking an oil-water emulsion with waste-pickling acid solution, and thereafter converting the iron ions present in the waste-pickling solution to magnetite particles which absorb the oil.

10 The magnetite particles and oil absorbed thereon are separated from the solution leaving a clarified solution.

Moser et al separates organic and aqueous phases by treatment of the emulsions with diatomaceous earth at an elevated temperature.

Weiss et al describes the use of a finely divided particulate mineral or clay material, the individual particles of which have been treated to produce a thin hydroxylated surface layer having a positive zeta potential at the adsorption pH.

None of the aforementioned references teach or suggest the use of organoclays to break emulsions of organic compositions and water or polar fluids.

25 Additionally, organoclays are well-known in the art, see for example the following U.S. patents:

2,531,427 to Hauser;
2,966,506 to Jordan;
3,422,185 to Kuritzke;
3,974,125 to Oswald;
4,081,496 to Finlayson; and
4,105,578 to Finlayson et al

None of these aforementioned references teach or

suggest the use of these organoclays to break emulsions of organic compositions and water or polar fluids.

Summary and Objects of the Invention

5 A method is provided for breaking emulsions of an organic composition and water or polar fluids. The method comprises contacting the emulsion with an emulsion-breaking amount of an organoclay to adsorb a major portion of the organic composition. Subsequently, a portion of the organoclay or water may be removed.

10 It is thus an object of this invention to provide a method of treating fluid waste, e.g., pools, streams, etc. to break the emulsions contained therein to facilitate disposal.

15 It is a further object of this invention to provide a method of treating both aqueous and polar fluid wastes containing such organic contaminants to facilitate disposal.

20 It is a further object of this invention to provide a method of treating fluid waste containing organic contaminants emulsified therein to "break" the emulsion, to permit removal of water to reduce the volume.

25 It is a further object of this invention to provide a method of treating fluid waste containing toxic organic contaminants emulsified therein to break the emulsion to permit the incineration or solidification of the toxic organics.

Brief Description of the Figure

Figure 1 shows the relationship of the logarithm of the distribution coefficient of certain organic con-

taminants with the logarithm of their solubilities in water.

Detailed Description of the Invention

Organoclays are well known in the art as exemplified by the aforementioned patents to Hauser, Jordan, Kuritzkey, Oswald et al, Finlayson, and Finlayson et al, the entire disclosures of which are incorporated herein by reference. In this invention, the term "organoclay" refers to various clay types, e.g. smectites, that have organo ammonium ions substituted for cations between the clay layers. The term "organo ammonium ion substituted" refers to a substituted ammonium ion in which one or more hydrogen atoms are replaced by an organic group. The organoclays are essentially solid compounds that have an inorganic and an organic phase.

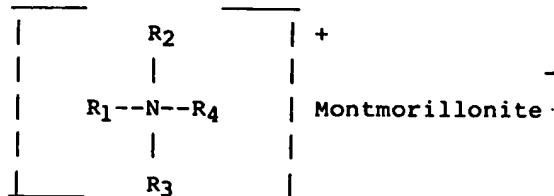
The preferred clay substrates for use in this invention are the smectite type clays, particularly the smectite type clays which have a cation exchange capacity of at least 75 millequivalents per 100 grams of clay. Useful clays for such purposes include the naturally occurring Wyoming variety of swelling bentonite and similar clays, and hectorite, which is a swelling magnesium-lithium silicate clay. The clays, are preferably converted to the sodium form if they are not already in this form. This can be effected, by a cation exchange reaction with a soluble sodium compound. These methods are wellknown in the art. Smectite-type clays prepared synthetically can also be utilized, such as montmorillonite, bentonite, beidelite, hectorite, saponite, and stevensite.

The organoclays useful in this invention include

those set forth in U.S. Patent No. 2,531,427 to Hauser.
These organoclays are modified clays which exhibit in
organic liquids, some of those characteristics which
untreated clays exhibit in water. For example, they
5 will swell in many organic liquids and will form stable
gels and colloidal dispersions.

Generally, the quaternary ammonium salt substituted
onto the clay has organic groups attached to the clay
which will range from aliphatic hydrocarbon of from 1 to
10 24 carbons to aromatic organic molecules, such as benzyl
groups that could have a host of groups substituted on
the benzyl ring. The number of benzyl versus straight
chain hydrocarbons substituted on the ammonium ion can
vary from 3 to 0 (i.e. dimethyl dioctadodecyl 0:2, methyl
15 benzyl dioctadodecyl 1:2, dibenzyl dioctobenzyl 1:1,
tribenzyl octadecyl 3:1, methyl dibenzyl octadecyl 2:1).
The amount of alkyl ammonium salt substituted on the
clay can vary between 0.5% to 50%.

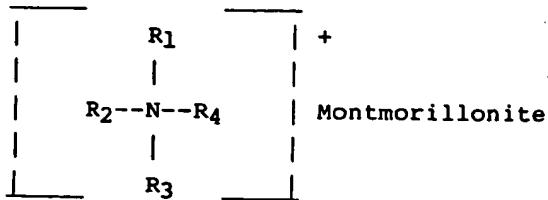
20 In particular, the preferred organoclay used in
this invention comprises one or more of the following
quaternary ammonium cation modified montmorillonite
clays:



25 wherein R₁ is an alkyl group having at least 10 carbon
atoms and up to, for example, 24 carbon atoms, and pre-
ferably having a chain length of from 12 to 18 carbon
atoms; R₂ is hydrogen, benzyl or an alkyl group of at
least 10 carbon atoms and up to, for example, 24 carbon

atoms, and preferably from 12 to 18 carbon atoms; and R₃ and R₄ are each hydrogen or lower alkyl groups, viz., they contain carbon chains of from 1 to 4 atoms, and preferably are methyl groups.

5 Other organoclays utilizable in the invention include benzyl organoclays such as dimethyl benzyl (hydrogenated tallow) ammonium bentonite; methyl benzyl di-(hydrogenated tallow) ammonium bentonite; and more generally quaternary ammonium cation modified montmorillonite clays represented by the formula:



wherein R₁ is CH₃ or C₆H₅CH₂; R₂ is C₆H₅CH₂; and R₅ and R₄ are alkyl groups containing long chain alkyl radicals having 14 to 22 carbon atoms, and most preferably wherein 20 to 35% of said long chain alkyl radicals contain 16 carbon atoms and 60% to 75% of said long chain alkyl radicals contain 18 carbon atoms.

15 The montmorillonite clays which may be so modified are the principal constituents of bentonite rock, and 20 have the chemical compositions and characteristics described, for example, in Berry and Mason, "Mineralogy", 1959, pp. 508-509. Modified montmorillonite clays of this type (i.e. organoclays) are commercially available 25 from Southern Clay Products, Inc., Gonzales, Texas under such trade designations as CLAYTONE 34 and 40, and are available from NL Industries, Inc., New York, New York under such trade designations as BENTONE 27, 34, and 38. The preferred organoclays utilized in this invention,

are the higher dialkyl dimethyl ammonium organoclays such as dimethyl di(hydrogenated tallow) ammonium bentonite; the benzyl ammonium organoclays, such as dimethyl benzyl (hydrogenated tallow) ammonium bentonite; and 5 ethylhydroxy ammonium organoclays such as methylbis (2-hydroxyethyl) octodecyl ammonium bentonite.

The fluid waste, which may be an aqueous waste or a waste fluid whose carrier fluid is a polar composition, e.g. aliphatic alcohol, etc. contains an amount 10 of organic contaminant. Typical organic contaminants are the chlorinated organic compounds, e.g. DDT, BDD, DDE, 2, 4-dichloro-phenol, tetrachloroethylene, and other organics such as benzene, toluene, methylene chloride, chloroform, 1, 2 dichloroethane 1, 1, 1-trichloroethane, trichloroethylene, tetrachloroethylene, 2-nitrophenol, pentachlorophenol, dimethyl phthalate, Lindane, Arochlor-1254, ethyl benzene, HCP, parathion, dichlorobenzene, hexachlorocyclopentadiene, ethylparathion, 2, 4-dinitrotoluene, naphtalene, 20 pyrene, etc.

In the method of this invention, a sufficient amount of the organoclay is added to the aqueous or polar fluid composition to break the emulsion and absorb substantially all of the organic contaminants on the organoclay. Preferably, the amount of organoclay is at 25 least about one percent (1%) by weight of the amount of organic contaminant and most preferably at least about five percent (5%) by weight of the organic contaminant. If too little organoclay is used, the emulsion will not be sufficiently broken. The upper limit of organoclay is primarily dictated by cost. For general guidance, 30 however, about ten percent (10%) by weight of the amount of the organic contaminant is a preferred upper limit.

The organoclay is mixed thoroughly with the fluid

waste. The temperature at which the organoclay is mixed with the waste is not critical, with room temperature being preferred for obvious cost considerations.

The organoclay, upon mixing in the fluid waste,
5 swells as the organic contaminant molecules are sorbed into and onto the organoclay. The organoclay additionally fixes the organic contaminant compounds through adsorption involving partitioning of the organic molecules of the contaminant into the organoclay.

10 The organic molecules of the contaminant preferably partition into the organic phase of the organoclay versus the aqueous phase or polar fluid phase of the fluid. The magnitude of organic partitioning of a given organic molecule into the organoclay over, for example, the aqueous phase can be predicted qualitatively by the solubility of the organic molecule in the aqueous phase. That is to say, an organic molecule that is very insoluble, e.g. oil, in an aqueous phase will partition very strongly into the organoclay relative to a more soluble organic molecule. This partitioning phenomenon also follows chromatographic theory which allows precise predictions of how organic molecules will migrate through a bed of organoclay. Figure 1 shows the linear relationship of distribution co-efficients for several 15 key organic species with three types of organoclay. The distribution coefficients equals the amount of organic adsorbed in the clay divided by the amount left in solution times the volume of the solution divided by the mass of the clay. The aqueous solution contains the 20 organics listed in Figure 1. Generally, the amount in solution depends on solubility.

The organoclay when added to the fluid waste composition tends to break organic contaminant-water emulsions. The organoclays are very effective at breaking

emulsions at extremely low dose rates of organoclay. After the step of adding the organoclay, a portion of the water or polar fluid is removed, for example, by decanting or otherwise separating the fluid from the 5 composition. Such procedure substantially reduces the volume of the waste fluid. The breaking of the emulsion is particularly useful if the waste is to be solidified, for less mass must be solidified when water is removed, and this therefore provides for decreased cost in 10 transportation and disposal. The water can also be recovered for further use. Additionally, the water removal or decanting step provides for the waste being incinerated at considerable savings, since the BTU value of the waste has increased substantially by the 15 exclusion of water. Still further, the organics left in the waste mass can be recovered for reuse and the organoclay regenerated.

Thus, the method of this invention provides for several advantages which include substantially reducing 20 the volume and mass of a waste fluid. This yields substantial savings in transportation and disposal site costs. Additionally, the organic contaminant-water emulsion breaking by the use of the organoclays, permits water to be returned to the plant for further use. Removal of water also makes incineration more feasible 25 since the organic contaminant has a high BTU value.

Example I

The following Table contains examples of how the organoclay can break organic-water emulsions:

Table 1

Organoclay Applied to Breaking of
Organic Water Emulsions

Type of Emulsion	Composition (A)	Organoclay Dose (wt. % of A)	Percent of Water Re- covered
Texaco API Sepa- rator Sludge	60% organic, 40% water	2.5%	98%
Amoco API Sepa- rator Sludge	80% organic, 20% water	2.5%	95%
BFI Lagoon Hazardous Waste	1/3 solids, 1/3 organic, 1/3 water	2.5%	98%
Alcoa Rolling Mill Emulsion (oil emulsion from lubrication in fanning mills)	10% solids, 40% organic 50% water	7%	90%

The organoclay utilized in this example was a dimethyl di(hydrogenated tallow) ammonium bentonite product available from Southern Clay Products, Inc., Gonzales, Texas.

5 While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the present disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended thereto.

Claims

1. A method for breaking emulsions of an organic composition and water comprising contacting the emulsion with an emulsion-breaking amount of an organoclay to adsorb a major portion of the organic composition.
5
2. A method for breaking an emulsion of an organic composition and a polar composition comprising contacting the emulsion with an emulsion-breaking amount of an organoclay to adsorb a major portion of the organic composition.
10
3. The method of claims 1 or 2, further comprising removing a portion of the polar fluid or water.
4. The method of claims 1 or 2, wherein the organoclay is a higher dialkyl dimethyl ammonium organoclay.
- 15 5. The method of claims 1 or 2, wherein the organoclay is a benzyl ammonium organoclay.
6. The method of claims 1 or 2, wherein the organoclay is an ethylhydroxy ammonium organoclay.
7. The method of claims 1 or 2, wherein the amount of
20 organoclay is at least about 1% by weight of the amount of organic composition.
8. The method of claims 1 or 2, wherein the amount of organoclay is at least about 5% by weight of the amount of organic composition.

9. The method of claim 7, wherein the amount of organo-clay is a maximum of about 10% by weight of the amount of organic composition.
10. The method of claim 8, wherein the amount of organo-clay is a maximum of about 10% by weight of the amount of organic composition.

Method for Breaking Emulsions

Abstract

A method is provided for treating polar or aqueous fluid emulsions of an organic composition. The method 5 comprises contacting the emulsion with an emulsion-breaking amount of an organoclay to adsorb a major portion of the organic composition. Preferably, a portion of the water or polar fluid is then removed.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER: _____**

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.